

Towards Tailored Interphase Formation Utilizing Surface-Bound Benzylsulfonium Salts as Cationic Initiators

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Introduction

The level of interaction between fiber and matrix is of crucial importance to the overall properties in a composite material.¹ It is through this interaction that the properties of the fiber and matrix are transmitted. The interactions between reinforcement and matrix in a composite are facilitated by the presence of a microscopic interphase region. The interphase is generally composed of a polymer network formed by multilayer buildup of a coupling agent attached to the surface of the fiber into which the matrix can propagate and bond. This provides a structural lattice which allows for good energy transfer from the matrix to the reinforcement.² For composites utilizing glass fiber or fillers, silane coupling agents are most widely used. Silane coupling agents ($\text{RSi}(\text{OR})_3$), have functionality which can react with surface hydroxyls on the glass surface ($-\text{OR}'$), and an organic functionality ($-R$) that can react or interact with the matrix resin (epoxy, amine, vinyl). The interphase plays a dominant role in the fracture toughness properties of composites and in its response to aqueous and corrosive environments. Being able to develop tailored interphases will allow control of the overall properties of composites to optimize strength, modulus, and toughness.

Recently it has been shown that benzylium salts are excellent latent initiators for epoxy resins,³ vinyl ethers,⁴ and spiro orthocarbonates or bicyclo orthoesters.⁵ These initiators are not hygroscopic, dissolve more readily in epoxy resins and exhibit a longer shelf-life, compared to the commonly used BF_3 -MEA complex. This study centers on designed composite interphases based on using polymer synthesis to chemically link initiating groups to the fiber surface, promote radial growth of the interphase out from the surface, and finally initiate matrix cure. The approach is based on tailoring interphase formation before matrix cure, and should help to develop very strong interactions between the composite components. Our basic approach is illustrated in Figure 1. Novel benzylium salts have been synthesized which possess an alkyl ether tether tied

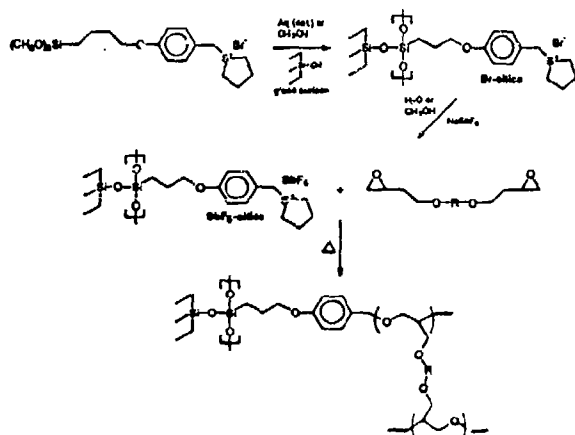


Figure 1: Polymerization of epoxy resins by surface-bound sulfonium salts.

to a reactive trialkoxysilane moiety capable of covalently bonding with glass surfaces. Here we report the coupling of sulfonium salts with high surface area silica gel as a model for glass fibers. High surface area silica was chosen due to the high loadings achievable which allow more facile characterization of the degree of functionalization. The ability of surface-bound sulfonium salts to initiate cationic polymerization of commercial epoxy resins will be discussed along with preliminary work with glass fiber reinforced systems.

Experimental

The benzylsulfonium salts synthesized are shown in Figure 2. Experimental procedures and characterization of the salts (except 1') along with all intermediates has been previously reported.⁷ Coupling of 3 to silica gel (as a model for glass fibers) will be reported in a future publication. Two different silica gels were used in this study. Merck silica gel-60 (silica) and Fisher Davisil grade 634 (davisil), with surface areas of 460 and 480 m²/g, respectively. The presence of sulfonium salt on the surface was confirmed by FTIR, ¹³C and ²⁹Si CP/MAS solid state NMR, and thermal gravimetric analysis (TGA).

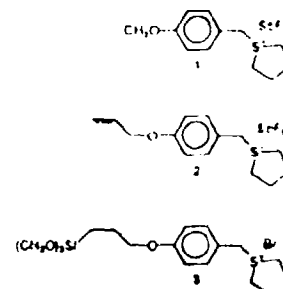


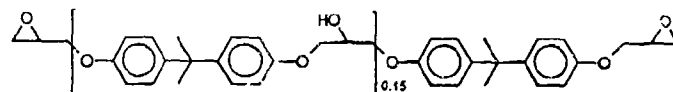
Figure 2: Benzylsulfonium salts

Characterization

Thermal analysis was performed using a TA instruments SUT 2960 (TGA) and DSC 2920, controlled using a TA Thermal Analyst 2100. TGA's were run at heating rates of 20 °C/min in air or N₂. DSC's were run at 10 °C/min with nitrogen purge. Solution ¹³C NMR were performed on a Bruker AC-200, solid state ¹³C and ²⁹Si CP/MAS were run on a Bruker MSL-400.

Results and Discussion

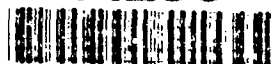
The ability of 1 to cure epoxy resins is demonstrated in Figure 3. The epoxy resins used were DER 331 (Dow Chemical, below) and DER 324 (which contains 17 wt % of a C₁₂-C₁₈ aliphatic glycidol



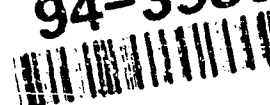
ether). The majority of epoxide reaction takes place below 150 °C and is attributed to cationic initiation and polymerization. However, at higher temperatures further reaction takes place, completing the matrix cure. Glass transition temperatures (T_g) and heats of reaction are given in Table 1. FTIR analysis indicated high conversion with the complete disappearance of the epoxy stretch at 915 cm^{-1} for both samples.

The ability of surface-bound sulfonium salts to cure epoxy resins was also investigated using DSC. Different weight percent formulations of treated silicas and epoxy resin were mixed at room temperature and subjected to DSC scans to 300°C. TGA on treated davisil indicated approximately 13% loading of sulfonium salt. Solid state ^{13}C CP/MAS NMR confirmed the structure of the coupled salt. The DSC thermogram for DER 331 with SbF_6 -davisil is shown in Figure 4 (Br-davisil shown as control). Values for heats of reaction and T_g 's are given in Table 1. As can be seen in Figure 4, only the

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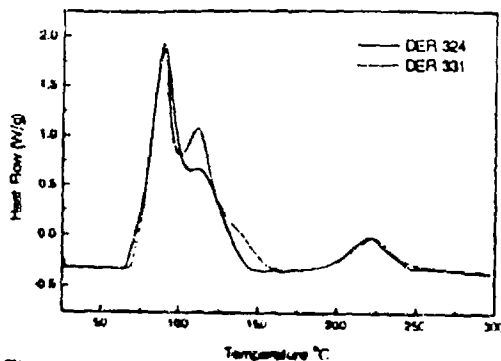


Figure 3: DSC thermograms for DER resins with 1 wt% 1.

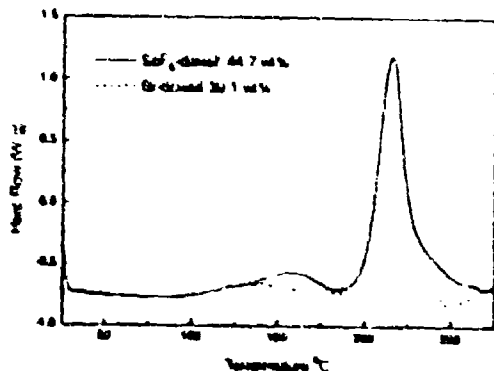


Figure 4: DSC thermogram for DER 331 with surface-bound sulfonium salts.

SbF₆-davisil showed any substantial exothermic behavior. However, no major polymerization appears to take place below 200 °C. The reduction of the lower exotherm for SbF₆-davisil/DER 331 relative to that seen with free initiator (Figure 3), indicates interference by the silica with the cationic mechanism of polymerization. This is similar to results previously reported by us.⁷ FTIR and ²⁹S CP/MAS solid state NMR on the modified silicas confirm the presence of residual Si-OH groups. The influence that surface hydroxyls have on the ability of 1 to polymerize DER 331 can be seen in Figure 5. Two

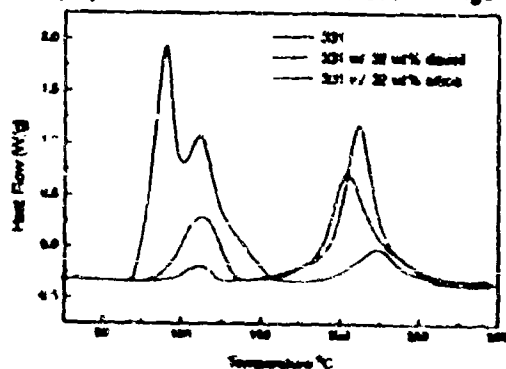


Figure 5: DSC thermograms for DER 331 (1 wt% 1) and unmodified silica gels.

exotherms are still seen for both silica gels, but the amount of reaction that occurs is greatly reduced with the lower temperature exotherm, showing a drastic reduction in the amount of heat liberated. The low T_g's observed on the second run for these samples also reflect the large drop in the amount of reaction (see Table 1).

High surface area silica, while allowing for a high degree of functionalization and thus more facile characterization, has many surface Si-OH groups that are left unreacted after functionalization. In addition, due to the hygroscopic nature of high surface area silica, obtaining reasonable dryness for cationic polymerization with this system is difficult. Therefore, lower surface area materials are being investigated as more appropriate models for glass fibers which will allow lower temperature cure to take place in higher yield.

Conclusions

The benzylium salts (1 and 2) both cured the epoxy resins to high conversion. In addition, the surface-bound initiators with SbF₆ counterion also cure epoxy resins whereas the Br salts will not. Quantitative determination of the extent of cure, concentration effects, surface effects, as well as physical properties of the cured materials are being investigated.

Acknowledgements

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Table 1

Initiator (wt%)	Resin	T _g (°C)	ΔH (J/g)	KJ/mol epoxy ^a	T _g
1 (1)	324	91	420	82	80
		230	61	12	
1 (1)	331	90	450	82	165
		224	65	12	
2 (1)	324	91	422	82	80
		228	139	27	
SbF ₆ -davisil (44.7%)	331	158	39 ^b	7	65
		216	234 ^c	43	
1 (1)	331	111	127 ^c	23	90
Davisil (32%)		205	253 ^c	45	
1 (1)	331	113	32 ^c	6	60
Silica (32%)		211	233 ^c	45	

a. Corrected for weight of heat.

b. Epoxy equivalent weight = 195 (DER 324), 182 (DER 331).

c. Obtained on DSC second scan.

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